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FRANK J. SEILER RESEARCH LABORATORY

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JULY 1982

**DENSITIES, ELECTRICAL CONDUCTIVITIES,
VISCOSITIES AND PHASE EQUILIBRIA OF
1,3-DIALKYLIMIDAZOLIUM CHLORIDE -
ALUMINUM CHLORIDE BINARY AND
TERNARY MELTS**

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PROJECT 2303

**AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE**

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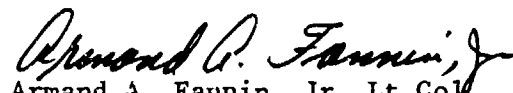
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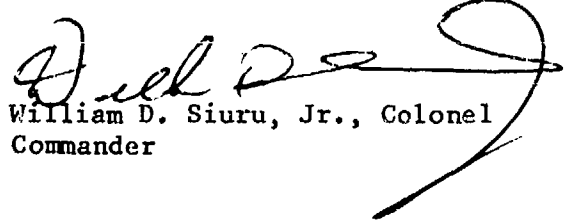
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ALUMINUM CHLORIDE BINARY AND TERNARY MELTS**

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SUMMARY

Experimental values are reported of the specific electrical conductivities, densities and kinematic viscosities of representative examples of binary 1,3-dialkylimidazolium chloride-aluminum chloride mixtures. The electrical conductivities of ternary mixtures of 1-methyl-3-ethylimidazolium chloride, aluminum chloride, and several organic and inorganic third components also are reported. All of these data were collected over wide temperature and composition ranges. The phase diagram for the 1-methyl-3-ethylimidazolium chloride-aluminum chloride system was determined.

PREFACE

Many binary compositions of 1,3-dialkylimidazolium chloride and aluminum chloride are ionic liquids which are liquid near (and in some cases well below) room temperature. They are potentially useful as electrolytes in batteries, for electroplating, and in photoelectrochemical cells. They have also been used as solvents in the investigation of a number of organic, organometallic, and inorganic solutes. The work described here is part of a continuing study designed to develop new low temperature electrolytes for battery applications. Experimental work is continuing, and theoretical modeling of the results is in progress. More complete results and their interpretation will be reported at a later date.

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INTRODUCTION

Molten salts have been considered as potential primary and secondary battery electrolytes for several years. As part of ongoing programs at the Frank J. Seiler Research Laboratory and the Air Force Aero-Propulsion Laboratory, we report here the specific electrical conductivities, densities, and kinematic viscosities of several binary mixtures of 1,3-dialkylimidazolium chloride and aluminum chloride over wide temperature and composition ranges. We also report the specific conductivities of certain 1-methyl-3-ethylimidazolium chloride (MeEtImCl)-aluminum chloride binaries to which several organic and inorganic compounds have been individually added. We have determined the phase diagram for the MeEtImCl-AlCl₃ binary system over most of the possible composition range.

One other major class of room temperature molten salts has been studied as a potential battery electrolyte and for other applications; that is the 1-alkylpyridinium chloride-aluminum chloride system. Extensive work has been done on this system in various laboratories. Studies in room temperature aluminum halide-containing melts in general were the subject of a recent review by Chum and Osteryoung (1). The present study parallels our early work on the densities, conductivities, and viscosities of the alkylpyridinium systems (2).

The dialkylimidazolium chlorides used in this study are shown below:



Compound	R ₁	R ₃
MeMeImCl	methyl	methyl
MeEtImCl	methyl	ethyl
MePrImCl	methyl	<u>n</u> -propyl
MeBuImCl	methyl	<u>n</u> -butyl
BuBuImCl	<u>n</u> -butyl	<u>n</u> -butyl

The rationale for the choice of these imidazolium salts has been discussed elsewhere (3), as has their synthesis and the preparation of the binary melts (4,5).

The third components which were added to the dialkyl imidazolium chloride-aluminum chloride binaries were acetonitrile, propionitrile, butyronitrile, benzene, xylene, and lithium chloride.

EXPERIMENTAL

Sample preparation.— The dialkylimidazolium salts and their binary mixtures with $AlCl_3$ were prepared as described elsewhere (4,5). Ternary mixtures were prepared by adding redistilled reagent grade third components to previously prepared binary melts (except for $LiCl$, which first was dried by prolonged heating just below its melting point). All sample preparation and handling (except in sealed dilatometers and viscometers) was conducted in a argon filled glove box (Vacuum/Atmospheres Company box and Model MO-40 DRI TRAIN), having moisture and oxygen concentrations less than 10 ppm.

Density measurements.— Densities were measured in sealed Pyrex dilatometric tubes whose volumes had been calibrated with mercury or distilled water in the conventional manner. Etched on each dilatometer was a reference mark midway up the stem (6). Samples which could be handled conveniently as liquids (except for the MeEtImCl binaries) were loaded into dilatometers with bulbs on the bottom of a relatively small diameter stem. The volume of this type of dilatometer to the reference mark was typically 6.5 cm^3 , and that of the stem typically $0.085 \text{ cm}^3/\text{cm}$. The remaining samples were loaded into straight tubes of typical volumes and cross sections of 1.5 cm^3 and $0.24 \text{ cm}^3/\text{cm}$, respectively.

Weighings were made inside the glove box. Loaded dilatometers were stoppered, removed from the glove box, evacuated, and sealed with a torch. The dilatometers were placed in a B. Braun Thermomix Model 1420 water bath, and temperatures monitored with an Air Force Standard Platinum Reference Thermometer. Estimated uncertainty in sample temperature was ± 0.05 °C. At temperatures below 20 °C and above 85 °C, the dilatometers were placed in the constant temperature bath described below in the viscosity section. The experimental measurements of sample volumes were made by measuring with a cathetometer the distance of the bottom of the meniscus from the reference mark. Cathetometer readings of the index mark and meniscus locations were made to an accuracy of ± 0.05 mm. Appropriate corrections were made in calibration and sample measurements for bouyancy, thermal expansion, and meniscus shape effects. Overall precision in density was estimated to be $\pm 0.1\%$ and $\pm 1\%$ for samples in the large and small dilatometers, respectively.

Conductivity measurements.— The same conductance cell was used for all samples, and is shown in Fig. 1. It was a Pyrex capillary approximately 0.5 cm long with a nominal i.d. of 0.05 cm. The capillary was sealed to a 0.6 cm i.d. Pyrex tube. Bright platinum wire coils were placed inside the larger Pyrex tube, immediately above the capillary, and on the outside surface of the capillary. A thermocouple was also inserted into the larger Pyrex tube. The assembly was immersed to approximately the same depth in small containers of each sample. Before each filling the cell was carefully cleaned by washing with acetonitrile and water and was dried in a 100 °C oven.

The conductance cell was calibrated at 25 °C using 0.1 demal aqueous KCl (7). The cell constant was 214.93 cm^{-1} , and was corrected for thermal expansion as appropriate for each individual experimental measurement.

Conductivity measurements were made at 1 kHz with a Beckman Model RC-18A conductivity bridge. Measurements at 1 kHz and 3 kHz were identical within experimental error, so no frequency corrections were considered necessary.

The sample containers were loaded and the conductance measurements made in the glove box. The containers were immersed in a well stirred mineral oil bath to a depth where the surface of the sample was at least 5 cm below the surface of the oil, in order to minimize temperature gradients within the sample. Temperature stability of at least ± 0.05 °C was attained over the entire temperature range, and the actual temperatures were known to within ± 0.1 °C. A Bayley Model 124 proportional temperature controller was used. Overall precision in specific conductivity was estimated to be $\pm 1\%$.

Viscosity measurements.- A closed, submersible, all Pyrex viscometer was employed, and is shown in Fig. 2. The viscometer could be opened for emptying, cleaning, and refilling, then resealed. The viscometer was calibrated at various temperatures with cyclohexanol, ethylene glycol, and glycerol. Flow times for calibration varied between 19 and 4550 s. The calibration data were fit to a straight line passing through the origin of a time-kinematic viscosity plot. The average deviation of calibration data from the line was $\pm 1\%$.

The viscometer was mounted on a vertical platform submerged in a well stirred silicone oil bath. The platform could be rotated in the vertical plane by remote control to fill the upper chamber of the viscometer. The passage of the liquid meniscus past two arrow marks above the capillary was timed with a precision of better than $\pm 1.5\%$ with a stop watch. At least six runs were made for each sample at each temperature, and the mean efflux times were used in the calculation of kinematic viscosity.

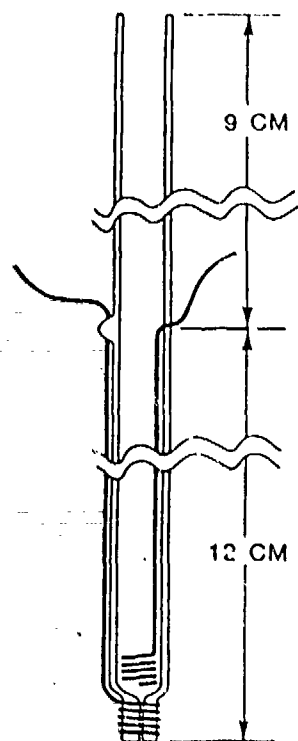


Fig. 1. Conductivity cell.

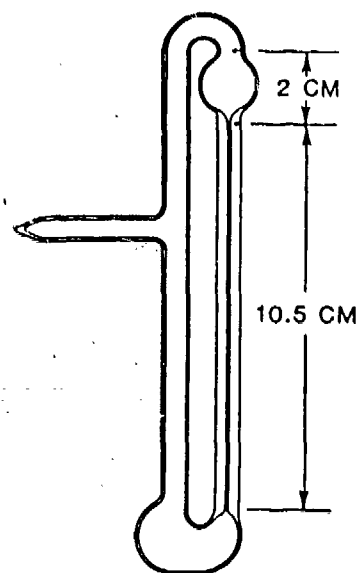


Fig. 2. Viscometer.

The oil bath was equipped with submerged heaters, but the principal temperature control was achieved with submerged coils attached to a NESLAB Endocal Model RTE-9B refrigerated circulating bath. The oil bath could be maintained at temperatures ranging from -15°C to 100°C with a long term stability of $\pm 0.5^{\circ}\text{C}$. The actual sample temperatures were known to within $\pm 0.1^{\circ}\text{C}$ at near ambient temperatures and $\pm 0.5^{\circ}\text{C}$ at the temperature extremes. On combining the above uncertainties with those in composition and misalignment of the capillary from the vertical, an overall error in kinematic viscosity of $\pm 2.5\%$ was estimated.

Melting and freezing point measurements.— The solid-liquid phase transitions, and in some cases glass transitions were measured by two methods; visually and by differential scanning calorimetry (DSC). Since most tran-

sitions were at sub-ambient temperatures, a conventional melting point apparatus could not be used for the visual determinations. A temperature controlled dewar (Wilmad WG-821 variable temperature insert, WG-836 transfer dewar, and WG-838 heater) designed for an electron paramagnetic resonance (epr) cavity proved to be convenient for measurements to -100°C . Samples were sealed in quartz epr tubes and their temperature was controlled by a stream of dry N_2 gas cooled by a glass coil immersed in liquid N_2 . The phase transitions were observed with a magnifying glass through the double quartz walls of the dewar. Many of the samples supercooled, so melting points, rather than freezing points, were taken as the true transition temperature. Glass transitions were clearly distinguished by an increase in viscosity with cooling, terminated by a sudden fracturing of the melt at the glass transition temperature.

The differential scanning calorimetry was done on a Perkin-Elmer DSC-2 calorimeter fitted with the sub-ambient accessories. Temperatures below 30°C were attained using liquid nitrogen cooling with a helium purge of the DSC head. The instrument was calibrated with acetone and with water before and after each set of experiments. The samples were contained in stainless steel large-volume pans which were loaded and sealed inside a glove box. The temperature was scanned at 10 or $20^{\circ}\text{C}/\text{min}$.

Most compositions were observed both visually and by DSC. The two methods usually agreed within less than $\pm 1^{\circ}\text{C}$, with an estimated "worst case" error of $\pm 2^{\circ}\text{C}$.

RESULTS AND DISCUSSION

The concentrations of binary melts are expressed as the "apparent mole fraction" of AlCl_3 . This is the melt composition calculated as though the melt were comprised of monomeric AlCl_3 and the appropriate imidazolium chloride. In fact, however, probably no measureable AlCl_3 exists in these melts (8); they are comprised of imidazolium cations and Cl^- , AlCl_4^- , and Al_2Cl_7^- anions. The molecular weight of the binary melts is given by

$$M = M_I + 133.34 \times N / (1-N) \quad (1)$$

where M_I is the molecular weight of the dialkylimidazolium chloride and N is the apparent mole fraction of AlCl_3 . Notice that this is not the customary formula for the evaluation of the molecular weight of a binary molten salt mixture; rather it allows for the fact that the number of ions present in the mixture is governed solely by the number of moles of imidazolium chloride present, and is not changed by the addition of AlCl_3 (9).

Concentrations of species in ternary melts are expressed as though a third component were added to an existing binary melt (which, in fact, is how they were prepared). Aluminum chloride concentration is expressed as the apparent mole fraction in the original binary, as defined above. The mole fraction of the third component, X_3 , was calculated from

$$X_3 = \text{moles}_{\text{third}} / (\text{moles}_{\text{third}} + \text{moles}_{\text{binary}}) \quad (2)$$

where the moles of binary can be calculated from its mass and eq. 1. Here again, the third component does not contribute to the production of ionic species. In the case of added LiCl, the third component does contribute ionic species, and this method of expressing concentrations is no longer suitable for making comparisons. (The actual mole fraction of LiCl in the one ternary melt studied was 0.052, whereas eq. 2 would have yielded the value 0.15.)

The raw experimental data were converted into densities, specific conductivities and kinematic viscosities, and are presented for the binary melts in Tables I, II, and III, respectively. Included in Tables I and II are the densities and conductivities of the pure 1,3-dialkylimidazolium chlorides. The viscosities of the pure salts and of the two lower AlCl₃ content binaries with MeMeImCl were not measured because of the experimental difficulties which were anticipated in working with these relatively high melting compounds in the present viscometer. It was not possible to work at an apparent mole fraction AlCl₃ higher than 0.666, for the melting temperature rose extremely rapidly with increasing AlCl₃ content in this composition region. Pure aluminum chloride is a non-electrolyte, and its physical properties are not considered here.

The specific conductivities of the ternary melts to which propionitrile has been added are given in Table IV. Densities and viscosities of the ternary mixtures have not been measured.

The MeEtImCl-AlCl₃ system was chosen as a "base-line" melt, primarily because of its relatively favorable conductivity and viscosity behavior and its wide liquid range, as shown below. Other studies are underway in our laboratory on nuclear magnetic resonance spectroscopy of this system and on the electrochemical behavior of a number of inorganic and organic solutes in MeEtImCl-AlCl₃ melts.

Table I. Densities of 1,3-Dialkylimidazolium Chloride-Aluminum Chloride Binary Melts.^a

T	DENSITY	T	DENSITY	T	DENSITY
N = 0.00		144.24	1.2470	59.20	1.1901
R ₁ = METHYL R ₃ = METHYL		151.80	1.2417	69.20	1.1928
127.24	1.1400	N = 0.66		79.60	1.1858
135.73	1.1283	R ₁ = METHYL R ₃ = METHYL		89.20	1.1792
144.24	1.1268	11.35	1.4173	100.70	1.1716
151.85	1.1254	18.95	1.4102	20.80	1.2192
N = 0.33		29.69	1.4001	31.10	1.2140
R ₁ = METHYL R ₃ = METHYL		39.73	1.3908	40.40	1.2074
151.80	1.2012	49.90	1.3816	50.90	1.1994
144.24	1.2072	59.37	1.3729	59.90	1.1954
135.75	1.2224	69.48	1.3637	69.40	1.1820
127.19	1.2271	82.60	1.3523	79.20	1.1809
69.43	1.2688	N = 0.00		N = 0.36	
80.23	1.2562	R ₁ = METHYL R ₃ = ETHYL		R ₁ = METHYL R ₃ = ETHYL	
70.19	1.2642	91.33	1.1090	9.40	1.2500
60.08	1.2740	93.48	1.1119	24.60	1.2364
N = 0.50		84.92	1.1237	32.40	1.2307
R ₁ = METHYL R ₃ = METHYL		72.90	1.1282	40.60	1.2376
59.14	1.3080	55.59	1.1396	49.90	1.2248
64.56	1.3017	43.49	1.1474	59.60	1.2182
69.60	1.3007	31.01	1.1632	70.50	1.2088
70.19	1.2977	N = 0.31		79.60	1.2021
70.89	1.2973	R ₁ = METHYL R ₃ = ETHYL		89.10	1.1977
80.21	1.2890	9.40	1.2227	100.70	1.1905
82.44	1.2905	24.60	1.2164	20.80	1.2426
82.47	1.2878	32.40	1.2091	31.10	1.2369
127.26	1.2637	40.70	1.2166	40.40	1.2285
135.70	1.2556	49.90	1.2094	50.90	1.2179

Table I. (Continued)

T	DENSITY	T	DENSITY	T	DENSITY
N = 0.42					
R ₁ = METHYL R ₃ = ETHYL					
9.40	1.2481	100.70	1.2259	N = 0.56	
24.60	1.2388	20.80	1.2817	R ₁ = METHYL R ₃ = ETHYL	
32.30	1.2333	31.10	1.2697	9.50	1.3383
40.70	1.2447	40.40	1.2667	23.70	1.3220
49.90	1.2346	50.90	1.2578	32.20	1.3159
59.80	1.2293	59.90	1.2501	40.70	1.3106
71.20	1.2115	69.40	1.2430	50.00	1.3048
79.70	1.2053	79.20	1.2331	60.10	1.2928
89.10	1.2042	N = 0.51		71.50	1.2802
100.70	1.1933	R ₁ = METHYL R ₃ = ETHYL		79.80	1.2717
20.80	1.2510	9.50	1.3039	89.30	1.2655
31.10	1.2490	23.70	1.2909	100.70	1.2594
40.40	1.2426	32.20	1.2841	20.80	1.3324
50.90	1.2347	40.70	1.2787	50.90	1.3039
59.90	1.2286	50.00	1.2688	69.40	1.2884
69.40	1.2211	60.00	1.2655	N = 0.61	
79.20	1.2153	71.50	1.2595	R ₁ = METHYL R ₃ = ETHYL	
N = 0.48		79.80	1.2461	9.60	1.3629
R ₁ = METHYL R ₃ = ETHYL		89.10	1.2399	23.70	1.3498
9.50	1.2896	100.60	1.2392	32.10	1.3413
23.70	1.2828	20.80	1.3016	40.70	1.3356
32.30	1.2740	31.10	1.2911	50.00	1.3277
40.70	1.2674	40.40	1.2845	50.20	1.3194
50.00	1.2600	50.90	1.2762	71.60	1.3091
59.90	1.2524	59.90	1.2617	79.80	1.3020
71.30	1.2442	69.40	1.2536	89.40	1.2934
79.70	1.2456	79.20		100.70	1.2856
89.20	1.2365			20.80	1.3591
				50.90	1.3303
				69.40	1.3195

Table I. (Continued)

T	DENSITY	T	DENSITY	T	DENSITY
N = 0.66		N = 0.33		N = 0.00	
R ₁ = METHYL R ₃ = ETHYL		R ₁ = METHYL R ₃ = PROPYL		R ₁ = METHYL R ₃ = BUTYL	
9.60	1.3942	11.28	1.2076	83.11	1.0867
23.60	1.3833	19.00	1.2021	70.12	1.0921
32.00	1.3754	29.23	1.1944	82.60	1.0806
40.70	1.3697	40.34	1.1871	69.48	1.0877
50.00	1.3645	50.36	1.1793	59.37	1.0967
60.10	1.3522	60.44	1.1730	49.92	1.1027
71.70	1.3385	70.22	1.1664	39.73	1.1080
79.80	1.3315	81.36	1.1589	29.69	1.1133
89.40	1.3236			18.92	1.1202
100.70	1.3089	N = 0.50		11.35	1.1286
20.80	1.3796	R ₁ = METHYL R ₃ = PROPYL			
50.90	1.3583	11.28	1.2739	N = 0.33	
69.40	1.3418	19.02	1.2671	R ₁ = METHYL R ₃ = BUTYL	
		29.21	1.2593	82.26	1.1503
N = 0.00		40.34	1.2491	59.27	1.1595
R ₁ = METHYL R ₃ = PROPYL		50.39	1.2424	49.80	1.1629
11.36	1.1267	60.44	1.2341	40.09	1.1662
18.95	1.1230	71.40	1.2267	29.49	1.1711
29.70	1.1148	81.39	1.2179	19.15	1.1763
39.73	1.1061			11.38	1.1795
49.90	1.0987	N = 0.66			
59.37	1.0925	R ₁ = METHYL R ₃ = PROPYL		N = 0.50	
69.57	1.0867	11.26	1.3636	R ₁ = METHYL R ₃ = BUTYL	
70.22	1.0817	19.02	1.3565	69.17	1.2044
82.59	1.0766	29.21	1.3473	82.34	1.1946
83.09	1.0744	40.34	1.3373	59.29	1.2119
		50.36	1.3284		
		60.44	1.3197		

Table I. (Continued)

T	DENSITY	T	DENSITY	T	DENSITY
49.80	1.2182	33.84	1.1011	69.86	1.2157
40.11	1.2265	39.89	1.0967	82.39	1.2056
19.15	1.2424	50.11	1.0904		
11.37	1.2489	60.06	1.0838		
29.49	1.2342	60.11	1.0842		
		69.83	1.0780		
N = 0.66		70.14	1.0773		
R ₁ = METHYL R ₃ = BUTYL		80.23	1.0705		
		82.36	1.0698		
69.14	1.2950				
82.26	1.2837	N = 0.50			
59.29	1.3034	R ₁ = BUTYL R ₃ = BUTYL			
49.80	1.3117				
40.09	1.3204	11.35	1.1744		
29.49	1.3299	18.37	1.1690		
19.15	1.3391	33.64	1.1579		
11.38	1.3462	39.91	1.1534		
		50.13	1.1461		
N = 0.00		60.08	1.1391		
R ₁ = BUTYL R ₃ = BUTYL		60.14	1.1390		
91.33	0.9865	69.86	1.1321		
93.32	0.9853	70.19	1.1319		
83.86	0.9951	80.23	1.1245		
72.30	1.0014	82.39	1.1231		
55.03	1.0091				
43.26	1.0187	N = 0.66			
28.54	1.0313	R ₁ = BUTYL R ₃ = BUTYL			
N = 0.33		11.35	1.2639		
R ₁ = BUTYL R ₃ = BUTYL		18.37	1.2580		
11.34	1.1162	33.59	1.2446		
18.36	1.1116	39.91	1.2401		
		50.13	1.2317		
		60.11	1.2237		

^a Temperatures in deg. C; densities in g/cm³.

Table II. Specific Conductivities of 1,3-Dialkylimidazolium Chloride-Aluminum Chloride Binary Melts.²

T	K X 10 ²	T	K X 10 ²	T	K X 10 ²
N = 0.00				N = 0.33	
R ₁ = METHYL R ₃ = METHYL				R ₁ = METHYL R ₃ = ETHYL	
153.1	10.872	79.6	4.2527	104.0	3.6624
157.0	11.603	100.0	5.5252	83.7	2.3805
159.3	12.015			21.4	0.2071
161.4	12.396	N = 0.00		40.3	0.5716
163.7	12.840	R ₁ = METHYL R ₃ = ETHYL		59.6	1.2109
		110.4	3.7466	79.3	2.1373
		100.3	2.8445	99.9	3.3849
		90.1	2.0600		
		79.7	1.4030		
		75.9	1.1992		
N = 0.33		71.5	0.9903	N = 0.34	
R ₁ = METHYL R ₃ = METHYL		67.7	0.8259	R ₁ = METHYL R ₃ = ETHYL	
79.6	2.5371	63.9	0.6818	99.8	3.5064
83.9	2.8256	59.8	0.5453	79.5	2.2694
89.8	3.2202	56.4	0.4480	59.7	1.3097
94.0	3.5284	52.1	0.3417	40.0	0.6473
100.1	4.0208	98.0	2.6646	22.0	0.2587
106.2	4.5255	102.4	3.0217		
		106.3	3.3705		
		110.3	3.7355		
N = 0.50		90.1	2.0594	N = 0.36	
R ₁ = METHYL R ₃ = METHYL		86.5	1.8157	R ₁ = METHYL R ₃ = ETHYL	
79.2	6.2741			22.1	0.3317
89.7	7.1910	N = 0.30		40.4	0.7829
100.0	8.1137	R ₁ = METHYL R ₃ = ETHYL		59.8	1.5177
109.8	8.9978	36.0	0.3557	79.7	2.5425
		38.4	0.4081	100.2	3.8522
N = 0.66		42.2	0.4951		
R ₁ = METHYL R ₃ = METHYL		46.0	0.5946		
20.4	1.3058	50.0	0.7092		
40.3	2.1389	53.9	0.8293		
59.8	3.1218	57.7	0.9580		

Table II. (Continued)

T	K X 10 ²	T	K X 10 ²	T	K X 10 ²
N = 0.40		N = 0.48		N = 0.51	
R ₁ = METHYL R ₃ = ETHYL		R ₁ = METHYL R ₃ = ETHYL		R ₁ = METHYL R ₃ = ETHYL	
19.8	0.5174	19.2	1.5520	29.9	2.4899
23.3	0.6034	23.2	1.7376	40.3	3.0954
28.4	0.7507	23.3	1.7355	59.7	4.3653
34.3	0.9324	23.4	1.7429	79.5	5.8031
36.4	1.0067	23.2	1.7312	100.1	7.4094
16.1	0.4361	23.5	1.7447		
21.4	0.5564	23.4	1.7360		
27.0	0.7024	23.6	1.7471		
32.8	0.8808	23.4	1.7345		
38.5	1.0773	36.4	2.4181		
42.4	1.2295	40.2	2.6383		
47.9	1.4600	44.0	2.8568		
53.7	1.7215	48.0	3.1003		
61.4	2.1067	51.9	3.3232		
69.2	2.5306	55.9	3.5973		
77.3	3.0071				
85.3	3.5106				
N = 0.44		N = 0.49			
R ₁ = METHYL R ₃ = ETHYL		R ₁ = METHYL R ₃ = ETHYL			
31.1	1.3202	17.4	1.6651		
40.4	1.7275	40.3	2.8867		
59.6	2.7394	59.7	4.1375		
79.6	3.9987	79.7	5.5859		
100.2	5.4885	100.2	7.1985		
		N = 0.50			
		R ₁ = METHYL R ₃ = ETHYL			
		21.9	2.0965		
		40.4	3.1666		

Table II. (Continued)

T	K X 10 ²	T	K X 10 ²	T	K X 10 ²
36.4	2.3522	N = 0.40		90.2	0.4608
N = 0.64		R ₁ = METHYL R ₃ = ETHYL		79.7	0.2784
R ₁				75.7	0.2245
17.5	1.2789	21.1	0.2702	N = 0.33	
21.3	1.4136	40.2	0.6325	R ₁ = METHYL R ₃ = BUTYL	
40.3	2.1722	59.4	1.2066		
59.5	3.0722	79.6	2.0367	99.7	1.7604
79.5	4.1190	100.0	3.0679	79.1	1.0549
100.1	5.2782			60.0	0.5725
N = 0.66		N = 0.50		40.3	0.2483
R ₁ = METHYL R ₃ = ETHYL		R ₁ = METHYL R ₃ = PROPYL		36.7	0.2060
22.2	1.3732	100.0	5.4111	N = 0.50	
30.8	1.6849	79.6	4.0560	R ₁ = METHYL R ₃ = BUTYL	
44.3	2.2239	59.7	2.8665		
59.9	2.9270	40.3	1.8710	18.7	0.8232
83.8	4.1174	30.7	1.4488	40.4	1.5641
104.0	5.2178	25.9	1.2621	59.9	2.4136
N = 0.00		N = 0.60		79.8	3.4196
R ₁ = METHYL R ₃ = PROPYL		R ₁ = METHYL R ₃ = PROPYL		100.2	4.5864
69.6	0.3238	30.8	1.3455	N = 0.66	
73.6	0.5453	40.3	1.7041	R ₁ = METHYL R ₃ = BUTYL	
89.7	0.8592	59.5	2.5402		
100.0	1.2767	79.4	3.5402	23.2	0.8683
110.4	1.8017	100.0	4.6865	40.3	1.3495
121.0	2.4555	N = 0.00		18.1	0.7463
131.7	3.2260	R ₁ = METHYL R ₃ = BUTYL		59.7	2.0086
142.1	4.0713			79.4	2.7803
152.3	4.9950	110.3	1.0130	100.2	3.6793
		100.2	0.7022		

Table II. (Continued)

T	K $\times 10^2$	T	K $\times 10^2$
N = 0.00		99.3	2.6033
R ₁ = BUTYL R ₃ = BUTYL			
110.2	0.3001		
105.2	0.2587		
104.2	0.2398		
102.2	0.2219		
107.8	0.2716		
N = 0.33			
R ₁ = BUTYL R ₃ = BUTYL			
100.2	0.8042		
79.6	0.4531		
60.2	0.2288		
69.8	0.3260		
N = 0.50			
R ₁ = BUTYL R ₃ = BUTYL			
21.0	0.4339		
40.7	0.8231		
59.9	1.3398		
79.5	1.9866		
100.1	2.7808		
N = 0.66			
R ₁ = BUTYL R ₃ = BUTYL			
18.3	0.4861		
40.1	0.9099		
59.2	1.3799		
79.0	1.9511		

^a Temperatures in deg. C; specific conductivities in ohm⁻¹ cm⁻¹.

Table III. Kinematic Viscosities of 1,3-Dialkylimidazolium Chloride-Aluminum Chloride Binary Melts.^a

T	UISCOSITY	T	UISCOSITY	T	UISCOSITY
N = 0.66		0.36	9.4047	0.61	9.5512
R ₁ = METHYL R ₃ = METHYL		N = 0.42		0.61	7.6605
0.66	13.826	R ₁ = METHYL R ₃ = ETHYL		0.61	6.3265
0.66	8.3787	0.42	73.041	0.61	5.1933
0.66	5.5695	0.42	46.698	0.61	4.4776
0.66	3.9817	0.42	30.099	0.61	3.9084
0.66	3.2489	0.42	21.154	0.61	3.3832
N = 0.31		0.42	16.244		
R ₁ = METHYL R ₃ = ETHYL		0.42	13.337	N = 0.66	
0.31	656.89	0.42	9.7760	R ₁ = METHYL R ₃ = ETHYL	
0.31	306.25	0.42	7.8657	0.66	21.789
0.31	154.13	0.42	6.5222	0.66	15.212
0.31	81.212			0.66	11.505
0.31	51.049	N = 0.50		0.66	8.8673
0.31	34.531	R ₁ = METHYL R ₃ = ETHYL		0.66	7.1329
0.31	23.514	0.50	21.203	0.66	5.7894
0.31	17.282	0.50	15.751	0.66	4.8367
0.31	13.105	0.50	15.721	0.66	4.8367
N = 0.36		0.50	11.893	0.66	4.1038
R ₁ = METHYL R ₃ = ETHYL		0.50	9.3534	0.66	3.5176
0.36	252.36	0.50	7.6239	0.66	3.0535
0.36	127.55	0.50	6.4196		
0.36	72.213	0.50	5.4547	N = 0.33	
0.36	45.516	0.50	4.6999	R ₁ = METHYL R ₃ = PROPYL	
0.36	30.217	0.50	4.1210	0.33	3583.5
0.36	21.266			0.33	489.04
0.36	15.829	N = 0.61		0.33	124.26
0.36	11.381	R ₁ = METHYL R ₃ = ETHYL		0.33	48.415
		0.61	16.664	0.33	23.670
		0.61	12.306	0.33	16.464

Table III. (Continued)

T		VISCOSITY		T		VISCOSITY		T		VISCOSITY	
N = 0.50		R ₁ = METHYL R ₃ = PROPYL		N = 0.50		R ₁ = METHYL R ₃ = BUTYL		N = 0.50		R ₁ = BUTYL R ₃ = BUTYL	
0.50		56.989		0.50		26.179		0.50		186.40	
0.50		26.406		0.50		13.662		0.50		100.69	
0.50		14.265		0.50		9.0089		0.50		60.409	
0.50		7.9146		0.50		5.9726		0.50		39.450	
0.50		5.7161		0.50		4.9833		0.50		27.065	
0.50		4.7146						0.50		19.713	
N = 0.66		R ₁ = METHYL R ₃ = PROPYL		N = 0.66		R ₁ = METHYL R ₃ = BUTYL		N = 0.66		R ₁ = BUTYL R ₃ = BUTYL	
0.66		32.611		0.66		64.269		0.66		14.803	
0.66		15.682		0.66		33.641		0.66		11.554	
0.66		9.0871		0.66		16.713		0.66		9.3314	
0.66		6.2535		0.66		10.000		0.66		7.6214	
0.66		4.3726		0.66		6.3903		0.66		6.4001	
0.66		3.6153		0.66		4.5533					
				0.66		3.6446		N = 0.66		R ₁ = BUTYL R ₃ = BUTYL	
N = 0.33		R ₁ = METHYL R ₃ = BUTYL		N = 0.33		R ₁ = BUTYL R ₃ = BUTYL		0.66		85.985	
0.33		558.22		0.33		912.86		0.66		50.663	
0.33		270.78		0.33		259.10		0.66		32.537	
0.33		147.86		0.33		97.710		0.66		22.522	
0.33		86.669		0.33		40.843		0.66		16.293	
0.33		55.011		0.33		28.409		0.66		12.482	
0.33		37.398						0.66		9.6245	
0.33		26.650						0.66		7.7324	
0.33		19.786						0.66		6.4733	
								0.66		5.3985	
								0.66		4.5924	

^a Temperatures in deg. C; kinematic viscosities in centistokes.

Table IV. Specific Conductivities of 1,3-Dialkylimidazolium Chloride-Aluminum Chloride Binary Melts to which Propionitrile has been Added.^a

T	$\kappa \times 10^2$	T	$\kappa \times 10^2$	T	$\kappa \times 10^2$
N = 0.32; X = 0.17					
14.4	0.3021	20.2	2.5796	17.1	5.1065
21.5	0.4935	40.3	3.8426	19.2	5.2744
40.5	1.0476	59.7	5.2186	40.1	6.5523
59.5	1.8472	79.8	6.7724	40.2	6.5804
79.4	2.7738	100.1	8.3739	40.3	6.5931
100.0	4.0999			59.6	7.7498
N = 0.33; X = 0.30					
31.2	1.0656	21.4	3.2555	59.8	7.7920
40.1	1.4121	40.2	4.5188	59.8	7.8702
59.3	2.2780	59.5	5.9447	79.4	9.0138
79.1	3.3529	79.4	7.5057	79.5	8.9799
99.5	4.7091	100.2	9.1592	79.6	9.1582
N = 0.33; X = 0.65					
22.5	2.3655	17.2	4.5284	89.9	9.6637
40.5	3.2637	30.8	5.5781	99.6	10.3807
59.8	4.3415	40.4	6.2607	99.7	10.3156
79.5	5.4721	40.5	6.1056	99.8	10.5227
100.1	6.7528	59.8	7.4952	99.8	10.5336
N = 0.33; X = 0.79					
21.5	3.0285	59.8	7.6369	99.9	10.5517
40.3	3.8969	79.4	9.0270	99.9	10.5600
59.9	4.8511	79.5	8.9239	N = 0.50; X = 0.91	
79.6	5.8457	99.8	9.7710	16.0	5.0273
99.0	6.8848	99.8	10.0625	17.5	4.7067
N = 0.50; X = 0.84					
31.2	1.0656	40.2	4.5188	30.8	5.2703
40.1	1.4121	59.5	5.9447	40.5	5.7761
59.3	2.2780	79.4	7.5057	59.8	6.6823
79.1	3.3529	100.2	9.1592	79.5	7.5986
99.5	4.7091			99.8	8.7525

Table IV. (Continued)

T	$\kappa \times 10^2$
N = 0.66; X = 0.28	
25.9	1.2878
40.0	1.8089
59.6	2.6485
79.3	3.6146
100.0	4.7194
N = 0.66; X = 0.38	
21.8	3.5350
40.3	4.5169
59.6	5.5935
79.7	6.6902
100.0	7.8250

^a Temperatures in deg. C; specific conductivities in $\text{ohm}^{-1} \text{cm}^{-1}$.

The freezing, melting, and glass transition data for MeEtImCl-AlCl₃ binaries are shown in Table V.

Table V. Solid-Liquid Phase Transition Temperatures for MeEtImCl-AlCl₃.^a

N	T	N	T	N	T
0.00	84	0.36	-68	0.56	-18
0.05	72	0.38	-72	0.58	-23
0.10	62	0.40	-75	0.60	-31
0.15	54	0.41	-27	0.61	-33
0.20	41	0.42	-24	0.62	-95
0.25	39	0.44	-19	0.64	-95
0.30	32	0.46	-10	0.66	-96
0.31	28	0.48	-3	0.68	45
0.32	21	0.50	7	0.70	79
0.33	19	0.52	-3	0.73	110
0.34	17	0.54	-9	1.00	195

^a Temperatures in °C.

The solid-liquid phase diagram for MeEtImCl-AlCl₃ binary melts is shown in Fig. 3. Qualitatively, the phase equilibria are similar to those reported by Hurley and Weir for 1-ethylpyridinium bromide - aluminum chloride binaries (10). They are not qualitatively similar to the chemically similar system NaCl-AlCl₃, as is evident from Fig. 3. All of the melting transitions are lower than for any previously reported chloroaluminate melts. In two regions the temperatures for the transitions abruptly became lower, then abruptly rose again. The transitions in these low temperature regions were glass transitions, and all attempts to induce true freezing for these compositions were fruitless. The glass transitions were clearly identified by DSC (slope change rather than a peak) and visually (fracturing of the melts rather than solid formation). The melting points for mixtures having aluminum chloride mole fractions greater than 0.666 were done in sealed tubes and presumably under significant AlCl₃ vapor pressure. No measurements were made on compositions greater than a mole fraction aluminum chloride of 0.73.

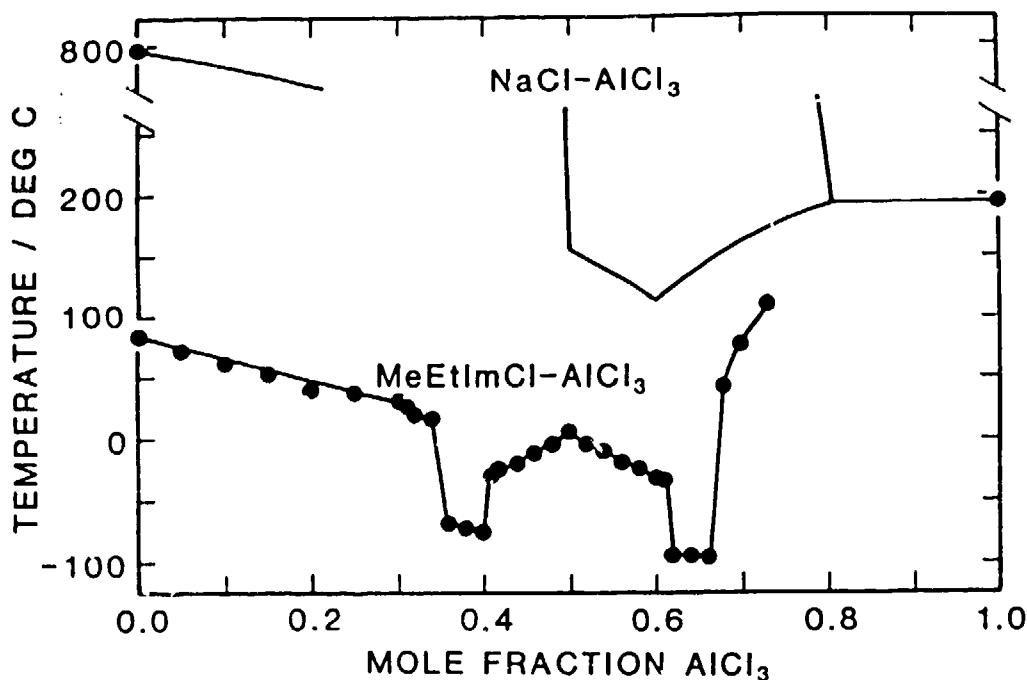


Fig. 3. Phase diagram for MeEtImCl-AlCl₃.

Experimental densities were least squares fitted to equations of the form

$$\rho = \rho_0 + \rho_1 (t - 60) \quad (3)$$

where t is the temperature in °C. The values of the fitted parameters are given in Table VI, together with the valid temperature range for each composition. No unusual features were found in the densities. As expected, there was a relatively smooth density decrease as the size of the imidazolium cation increased. This is illustrated in Fig. 4 for $N = 0.50$ melts at 60 °C; similar behavior was noted at other compositions and temperatures.

Table VI. Least Squares Fitted Parameters for Binary Melt Densities.^a

R ₁	R ₃	N	ρ_0	$\rho_1 \times 10^4$	T _{min}	T _{max}
METHYL	ETHYL	0.00	1.1378	-7.8253	31	91
METHYL	ETHYL	0.31	1.1955	-6.0420	-20	100
METHYL	ETHYL	0.36	1.2151	-6.8975	-20	100
METHYL	ETHYL	0.42	1.2244	-6.3662	-20	100
METHYL	ETHYL	0.48	1.2531	-7.0695	0	100
METHYL	ETHYL	0.51	1.2667	-7.6121	0	100
METHYL	ETHYL	0.56	1.2933	-8.9639	-11	100
METHYL	ETHYL	0.61	1.3205	-8.5937	-20	100
METHYL	ETHYL	0.66	1.3498	-9.0610	-20	100
METHYL	METHYL	0.00	1.1745	-5.5647	127	151
METHYL	METHYL	0.33	1.2739	-7.5142	60	152
METHYL	METHYL	0.50	1.3053	-6.7460	59	152
METHYL	METHYL	0.66	1.3725	-9.1391	11	83
METHYL	PROPYL	0.00	1.0918	-7.3377	11	83
METHYL	PROPYL	0.33	1.1734	-6.9507	11	81
METHYL	PROPYL	0.50	1.2348	-7.8879	11	81
METHYL	PROPYL	0.66	1.3198	-8.9647	11	81
METHYL	BUTYL	0.00	1.0965	-6.0315	11	83
METHYL	BUTYL	0.33	1.1590	-4.1182	11	82
METHYL	BUTYL	0.50	1.2113	-7.6234	11	81
METHYL	BUTYL	0.66	1.3030	-8.8205	11	82
BUTYL	BUTYL	0.00	1.0085	-6.7284	28	93
BUTYL	BUTYL	0.33	1.0841	-6.5641	11	82
BUTYL	BUTYL	0.50	1.1391	-7.1948	11	82
BUTYL	BUTYL	0.66	1.2237	-8.1797	11	82

^a Temperatures in °C; densities in g/cm³.

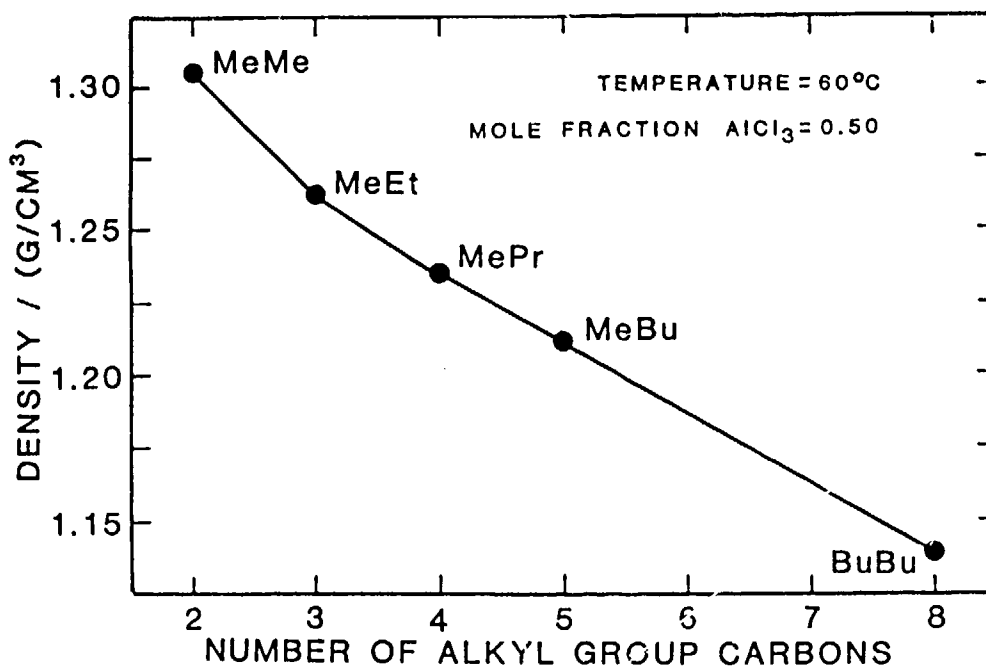


Fig. 4. Dependence of density on imidazolium cation size.

The composition dependence of the density of MeEtImCl-AlCl₃ melts at 60 °C is shown in Fig. 5. Density appears to be a monotonic function of AlCl₃ content. Similar behavior was observed for other temperatures. For MeEtImCl-AlCl₃ melts the density at each experimental composition and temperature was obtained by least squares fitting the methyl-ethyl binary densities in Table I (excluding pure MeEtImCl) to the equation

$$\rho = a_0 + a_1 (N - 0.5) + a_2 (N - 0.5)^2 + a_3 (t - 60) + a_4 (t - 60) (N - 0.5) \quad (4)$$

where the fitted values of the coefficients are $a_0 = 1.26229$, $a_1 = 0.456947$, $a_2 = 0.602142$, $a_3 = -7.67027 \times 10^{-4}$, and $a_4 = -8.97573 \times 10^{-4}$.

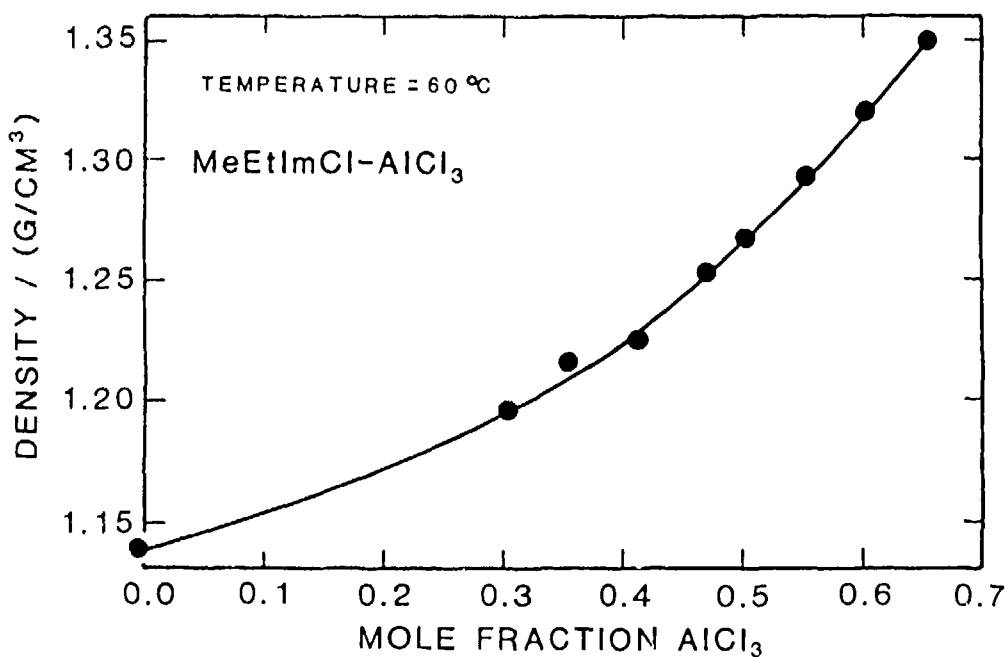


Fig. 5. Dependence of density on MeEtImCl-AlCl₃ melt composition.

We assumed the dependence of density upon AlCl_3 content would be similarly monotonic for the other four dialkylimidazolium chloride - AlCl_3 systems, and therefore measured densities only at AlCl_3 mole fractions 0.00, 0.33, 0.50, and 0.66.

Experimental specific conductivities were least squares fitted to equations of the form

$$\kappa = \kappa_0 + \kappa_1 (t - 60) + \kappa_2 (t - 60)^2 \quad (5)$$

The values of the fitted parameters are given in Table VII, together with the valid temperature range for each composition.

The dependence of specific conductivity on composition and temperature was not as simple as for density. The dependence on cation molecular weight was not as regular as for densities. A typical representation of this behavior can be seen in Fig. 6, where the conductivity of equimolar MeEtImCl-AlCl_3 is nearly as high as that of the corresponding dimethyl salt binary, and very substantially higher than that of the methyl-propyl analog. Similar behavior was noted at other temperatures and compositions, as shown in Figs. 7 and 8. These latter two figures clearly show that the specific conductivity is markedly dependent upon composition of the melt, with equimolar melts being the best conductors. The dibutyl system appears to be an exception to this at low temperatures, where the AlCl_3 rich melt is the better conductor. In the basic composition region, the relative decrease in conductivity for imidazolium rich compositions becomes greater at lower temperatures, as can be seen by comparing Figs. 7 and 8. (Missing data on these figures correspond to samples below their melting points.)

The effects of temperature and melt composition on the equivalent conductivity of MeEtImCl-AlCl_3 melts are shown on Fig. 9.

Table VII. Least Squares Fitted Parameters for Binary Melt Specific Conductivities.^a

R ₁	R ₂	N	K ₀ × 10 ²	K ₁ × 10 ⁴	K ₂ × 10 ⁶	T _{min}	T _{max}
METHYL	ETHYL	0.00	0.5485	3.0871	6.4687	52	110
METHYL	ETHYL	0.30	1.0401	3.6487	3.3282	36	58
METHYL	ETHYL	0.33	1.2276	4.0044	3.5180	21	104
METHYL	ETHYL	0.34	1.3301	4.1150	3.4135	22	100
METHYL	ETHYL	0.36	1.5267	4.4399	3.3882	22	100
METHYL	ETHYL	0.40	2.0239	5.0962	3.3497	16	85
METHYL	ETHYL	0.44	2.7631	5.7540	2.5818	31	100
METHYL	ETHYL	0.48	3.8661	6.7385	2.5529	19	56
METHYL	ETHYL	0.49	4.1523	6.7567	2.1262	17	100
METHYL	ETHYL	0.50	4.4799	7.0092	1.9378	22	100
METHYL	ETHYL	0.51	4.3883	6.8528	1.7390	30	100
METHYL	ETHYL	0.52	4.2454	6.6614	1.8959	18	106
METHYL	ETHYL	0.58	3.6404	5.9530	2.1441	36	58
METHYL	ETHYL	0.64	3.0935	4.8956	1.4423	17	100
METHYL	ETHYL	0.66	2.9277	4.6334	1.3382	22	104
METHYL	METHYL	0.00	-5.0593	15.8865	1.3204	153	164
METHYL	METHYL	0.33	1.4978	4.4066	4.6565	80	106
METHYL	METHYL	0.50	4.6324	8.4086	0.7210	80	110
METHYL	METHYL	0.66	3.1296	5.3115	1.7539	20	100
METHYL	PROPYL	0.00	0.2087	0.7552	4.8038	70	152
METHYL	PROPYL	0.40	1.2284	3.5281	2.7283	21	100
METHYL	PROPYL	0.50	2.8821	5.4980	2.1200	26	100
METHYL	PROPYL	0.60	2.5659	4.6650	1.6184	30	100
METHYL	BUTYL	0.00	0.1231	0.1456	3.2260	75	110
METHYL	BUTYL	0.33	0.5726	2.0957	2.2558	36	100
METHYL	BUTYL	0.50	2.4127	4.6523	1.9272	18	100
METHYL	BUTYL	0.66	2.0170	3.6113	1.3517	18	100
BUTYL	BUTYL	0.00	0.2515	-0.9381	2.0592	102	110
BUTYL	BUTYL	0.33	0.2268	0.8820	1.3791	60	100
BUTYL	BUTYL	0.50	1.3407	2.9590	1.6109	21	100
BUTYL	BUTYL	0.66	1.4003	2.6490	1.0825	18	100

^a Temperatures in °C; specific conductivities in ohm⁻¹ cm⁻¹

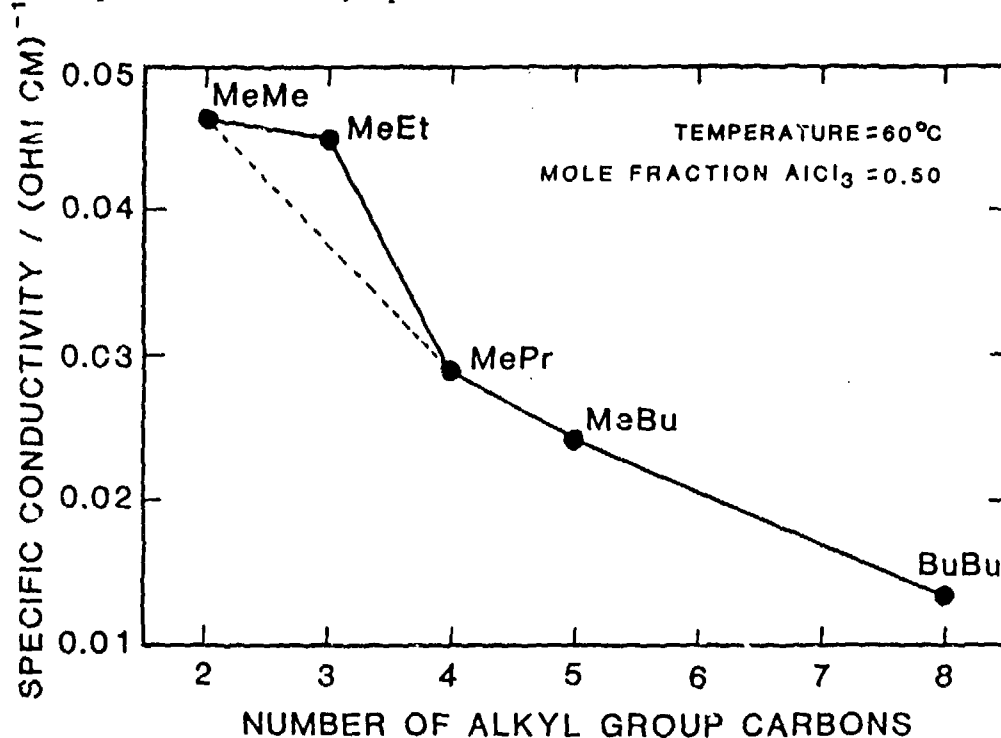


Fig. 6. Dependence of specific conductivity on imidazolium cation size.

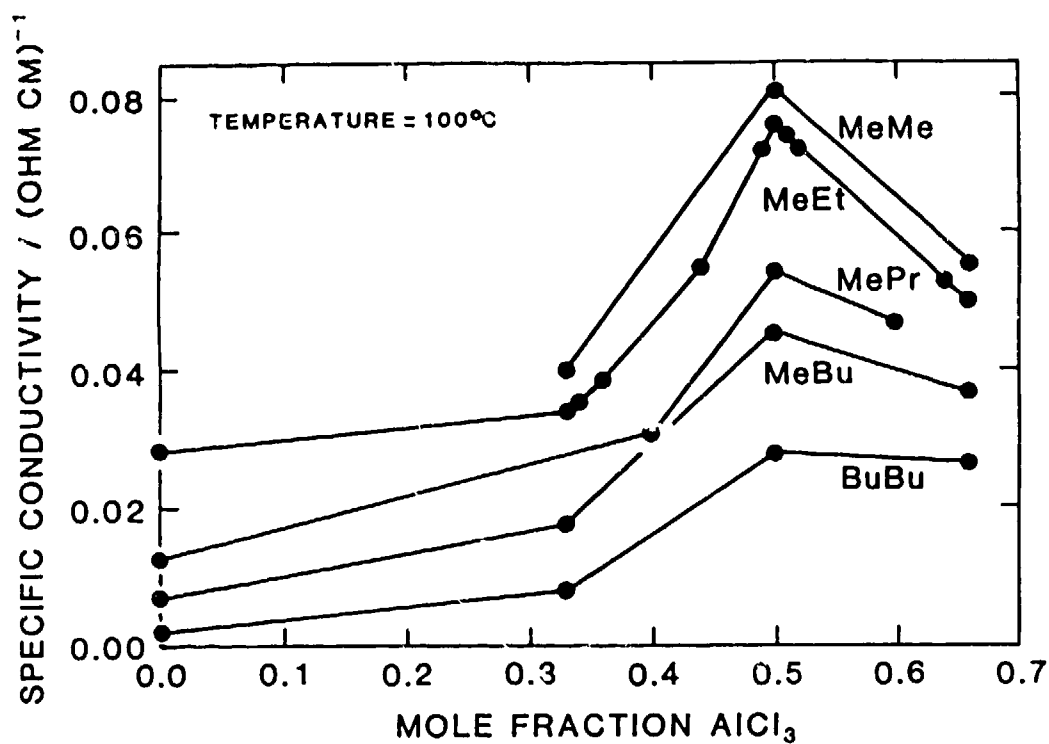


Fig. 7. Dependence of specific conductivity on $\text{R}_1\text{R}_3\text{ImCl-AlCl}_3$ melt composition at 100°C .

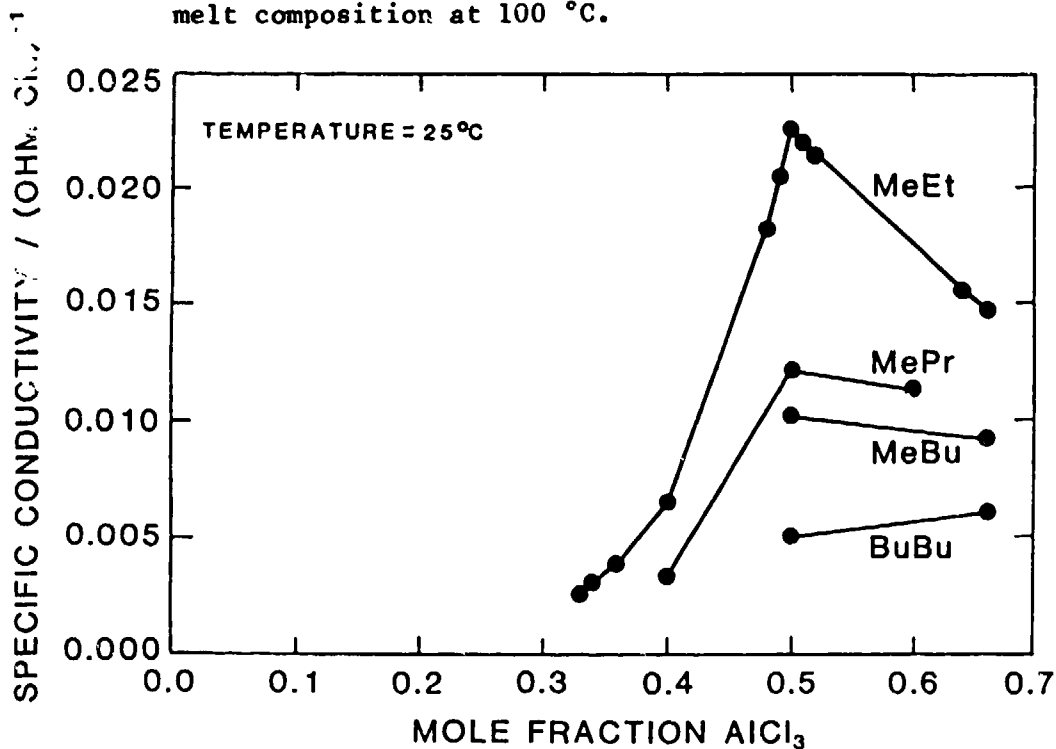


Fig. 8. Dependence of specific conductivity on $\text{R}_1\text{R}_3\text{ImCl-AlCl}_3$ melt composition at 25°C .

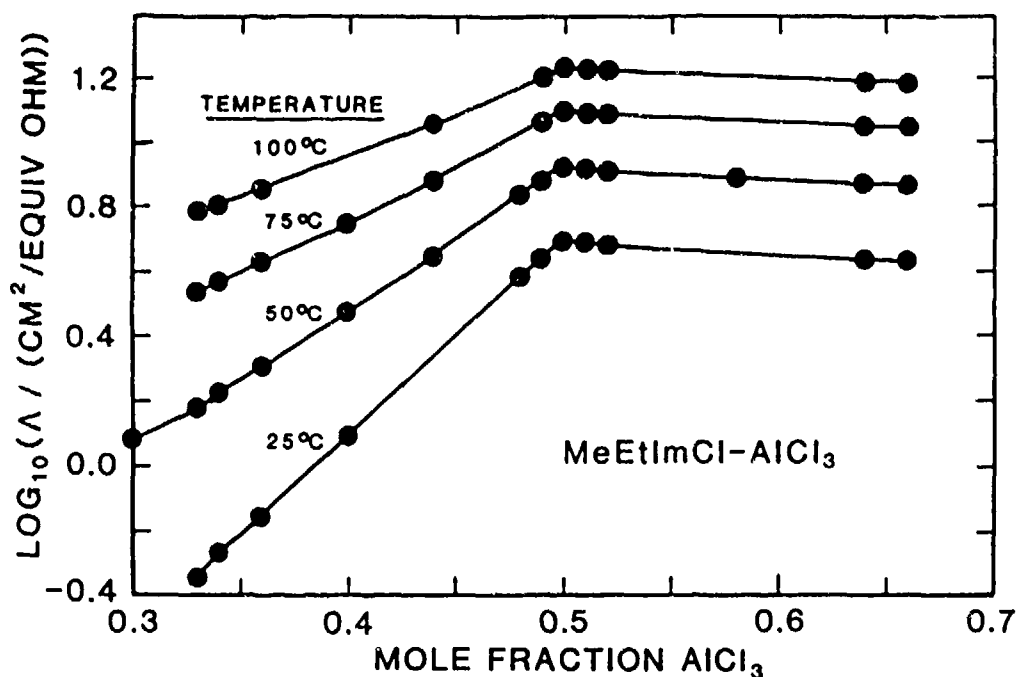


Fig. 9. Dependence of equivalent conductivity on MeEtImCl- AlCl_3 melt composition and temperature.

Work is now in progress on theoretically modeling the conductivities of these binary melts, so that the experimental results can be matched to equations derived from the transport model chosen. As was observed in 1-alkylpyridinium- AlCl_3 melts, the equivalent conductivities did not display Arrhenius behavior very satisfactorily. This work will be reported later.

The kinematic viscosities given in Table III were converted to absolute viscosities by

$$\eta = \rho \nu \quad (6)$$

The absolute viscosities of the MeEtImCl- AlCl_3 melts were determined using densities calculated from eq. 4. Kinematic viscosities of the remaining binary melts were measured at the same compositions at which their densities were

determined. Therefore densities used in eq. 6 for these melts were calculated from eq. 3.

The absolute viscosities were least squares fitted to equations of the form

$$\log_{10} \eta = \eta_0 + \eta_1/T + \eta_2/T^2 \quad (7)$$

where T is the temperature in kelvin. The values for the fitted parameters are given in Table VIII, together with the valid temperature ranges for each composition.

Table VIII. Least Squares Fitter Parameters for Binary Melt Absolute Viscosities.^a

R	R ₂	N	η_0	$\eta_1 \times 10^{-3}$	$\eta_2 \times 10^{-5}$	T _{min}	T _{max}
METHYL	ETHYL	0.31	7.9219	-6.1188	13.3555	10	90
METHYL	ETHYL	0.36	4.3579	-3.6006	8.7177	10	90
METHYL	ETHYL	0.42	2.0983	-1.8460	5.1268	10	90
METHYL	ETHYL	0.50	0.7459	-0.7565	2.7028	10	90
METHYL	ETHYL	0.61	0.8081	-0.8276	2.7888	10	90
METHYL	ETHYL	0.66	0.1483	-0.4269	2.1597	0	90
METHYL	PROPYL	0.33	8.0934	-6.2378	13.7205	11	81
METHYL	PROPYL	0.50	0.9359	-1.0397	3.5183	11	81
METHYL	PROPYL	0.66	1.5723	-1.3605	3.7797	11	81
METHYL	BUTYL	0.33	4.6591	-3.9661	10.0434	20	82
METHYL	BUTYL	0.50	2.5339	-2.0077	5.0078	20	82
METHYL	BUTYL	0.66	1.6208	-1.4008	3.9005	11	82
BUTYL	BUTYL	0.33	2.7968	-2.6367	7.9071	11	82
BUTYL	BUTYL	0.50	2.0506	-1.7679	4.8542	11	82
BUTYL	BUTYL	0.66	1.5038	-1.3622	3.9500	11	82

^a Temperatures in °C; absolute viscosities in cP.

As implied by eq. 7, the absolute viscosities did not exhibit Arrhenius behavior. This is in contrast to the 1-alkylpyridinium-AlCl₃ melts, which did obey the Arrhenius equation (over a somewhat smaller experimental temperature range) (3). The viscosities of the imidazolium melts were "mirror images" of their equivalent conductivities. Representative viscosities are shown in Fig. 10. The dependence of viscosity on the size of the dialkylimidazolium cation is even more anomalous than the conductivity behavior. Figure

11 shows that MeEtImCl-AlCl₃ melts have substantially lower viscosities than do the other melts studied. The theoretical modeling of transport phenomena cited above includes modeling of absolute viscosities.

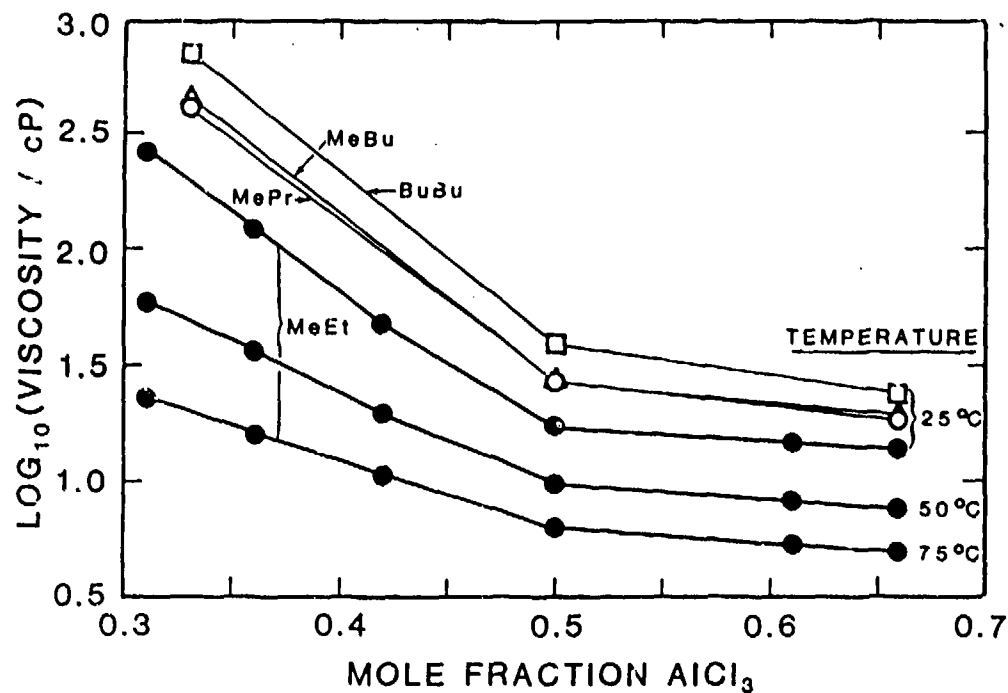


Fig. 10. Dependence of absolute viscosity on melt composition and temperature.

The experimental specific conductivities of the ternary melts (including those presented in Table IV) were least squares fitted to eq. 5, and the resulting parameters are given in Table IX, together with the valid temperature range for each composition. Addition of the relatively polar molecules acetonitrile and propionitrile to MeEtImCl-AlCl₃ binaries increased the specific conductivity. Butyronitrile produced a smaller but still significant improvement in conductivity. The conductivity increases presumably were due to the lowering of melt viscosities; viscosities of the ternary melts have not been measured, but the solutions appeared to the eye noticeably more fluid when they were handled.

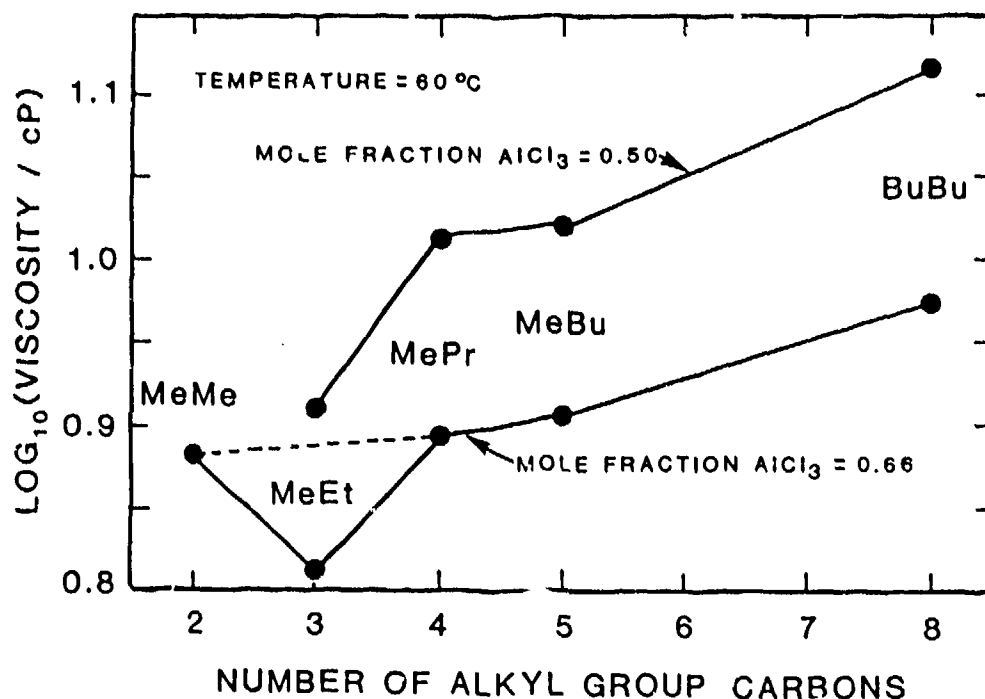


Fig. 11. Dependence of absolute viscosity on imidazolium cation size.

Additions of benzene had very little effect on conductivity, and xylene significantly lowered the conductivity. Only small amounts of LiCl markedly lowered the specific conductivity. Some of these effects may be seen in Fig. 12.

The organic cosolvents appeared to be soluble over large composition regions. They apparently were miscible in all proportions with the equimolar MeEtImCl-AlCl₃ binary melt at room temperature. The nitriles were miscible in all proportions with $N = 0.33$ melts. An immiscibility region was observed from $0.10 > X_2 > 0.33$ for propionitrile in the $N = 0.66$ binary melt. In basic melts LiCl was the only alkali chloride that had a substantial solubility (up to 0.1 mole fraction). In acidic melts all of the alkali chlorides were soluble up to at least 0.1 mole fraction, but many of the

resulting ternaries were no longer liquid at room temperature. Alkali chloride solubilities were sharply reduced in equimolar melts.

Table IX. Least Squares Fitted Parameters for Ternary Melt Specific Conductivities.^a

THIRD COMPONENT	N	X ₃	K ₀ × 10 ²	K ₁ × 10 ⁴	K ₂ × 10 ⁶	T _{min}	T _{max}
ACETONITRILE	0.33	0.72	3.1083	5.4505	-	18	80
PROPIONITRILE	0.33	0.17	1.8436	4.5419	2.5903	14	100
PROPIONITRILE	0.33	0.30	2.3086	5.0440	2.5715	31	100
PROPIONITRILE	0.33	0.65	4.3398	5.6359	0.9570	22	100
PROPIONITRILE	0.33	0.79	4.8528	4.9701	0.6041	21	99
BUTYRONITRILE	0.33	0.14	1.4721	4.2394	3.4535	27	116
BUTYRONITRILE	0.33	0.32	1.9577	4.6074	4.0041	28	100
ACETONITRILE	0.50	0.77	6.1811	7.5627	-	19	100
ACETONITRILE	0.50	0.77	7.3380	8.0714	-0.2533	17	100
ACETONITRILE	0.50	0.87	8.4408	9.1128	-	30	100
ACETONITRILE	0.50	0.93	9.6865	8.7136	-	18	100
PROPIONITRILE	0.50	0.21	5.2429	7.2817	1.4231	20	100
PROPIONITRILE	0.50	0.36	5.9837	7.5050	1.0658	21	100
PROPIONITRILE	0.50	0.75	7.5696	6.7759	-0.7188	17	100
PROPIONITRILE	0.50	0.84	7.7976	6.4320	0.6093	17	100
PROPIONITRILE	0.50	0.91	6.6727	4.7537	1.0422	16	100
BUTYRONITRILE	0.50	0.18	4.5765	7.0354	1.3607	29	100
BUTYRONITRILE	0.50	0.31	4.8747	7.0043	1.3644	35	100
BUTYRONITRILE	0.50	0.64	5.6268	6.6056	0.5578	30	99
BUTYRONITRILE	0.50	0.80	5.6351	5.1629	0.0991	30	99
BENZENE	0.50	0.64	5.1047	6.8984	1.1378	15	100
BENZENE	0.50	0.78	4.5274	4.8981	-	21	70
BENZENE	0.50	0.87	3.9348	3.8973	-	18	60
XYLENE	0.50	0.03	4.2946	6.7084	1.8978	17	100
XYLENE	0.50	0.23	4.2241	6.4675	1.4934	34	100
XYLENE	0.50	0.73	3.5247	4.6637	-	25	100
XYLENE	0.60	0.27	3.4723	5.2782	1.4164	18	100
PROPIONITRILE	0.66	0.28	2.6691	4.5585	1.4563	26	100
PROPIONITRILE	0.66	0.88	5.6048	5.4898	0.1561	22	100

^a Temperatures in deg. C; specific conductivities in ohm⁻¹ cm⁻¹.

The greatest conductivity improvements were with acetonitrile and propionitrile. At the highest temperatures reached in this study, acetonitrile evaporated rapidly out of the liquid phase, but propionitrile did not. The latter cosolvent therefore was chosen as the "base-line" third component. A detailed study is now underway of the density, conductivity, and viscosity of propionitrile in MeEtImCl-AlCl₃, within the composition matrix $0.46 < N \leq 0.54$ and $0 \leq X_3 \leq 0.75$.

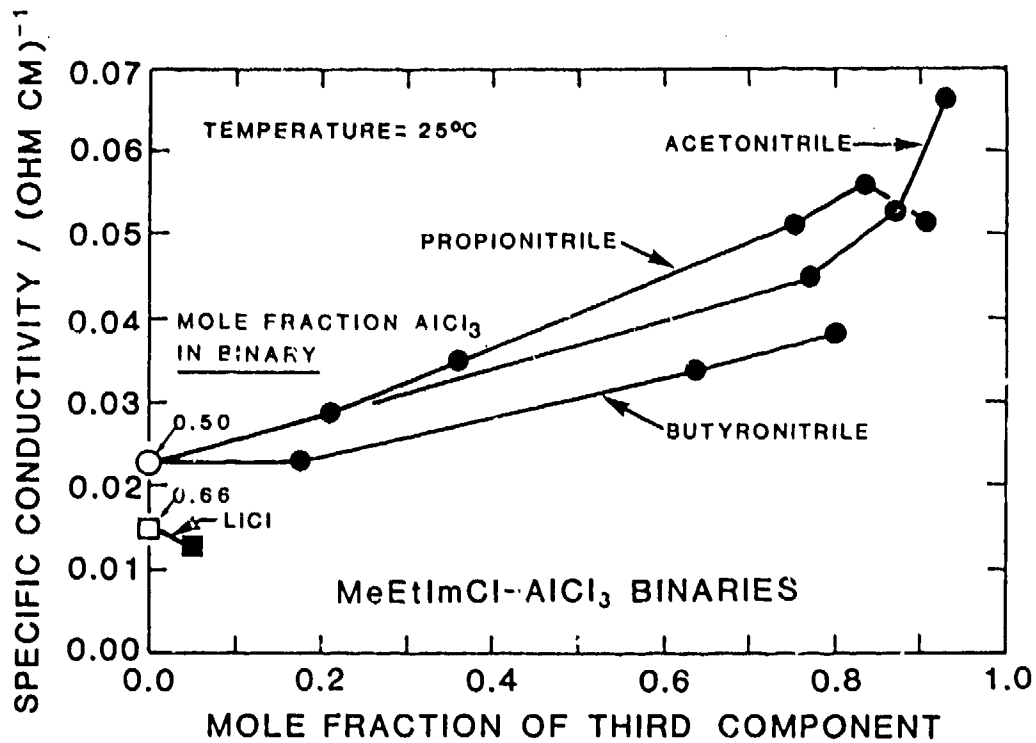


Fig. 12 Specific conductivity of ternary melts.

REFERENCES

1. H. Chum and R. A. Osteryoung, in "Ionic Liquids," D. Inman and D. Lovering, Editors, p. 407, Plenum Press, New York, NY (1981).
2. R. A. Carpio, L. A. King, R. E. Lindstrom, J. C. Nardi, and C. L. Hussey, J. Electrochem. Soc., 126, 1644 (1979).
3. J. S. Wilkes and C. L. Hussey, Frank J. Seiler Research Laboratory Technical Report FJSRL-TR-82-0002, USAF Academy, Colorado, 1982; ADA 111651.
4. J. S. Wilkes and J. A. Levisky, Frank J. Seiler Research Laboratory Technical Report FJSRL-TR-81-0001, USAF Academy, Colorado, 1981; ADA 094772.
5. J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, Inorg. Chem., 21, 1263 (1982).
6. L. A. King and D. W. Seegmiller, J. Chem. Eng. Data, 16, 23 (1971).
7. G. Jones and B. C. Bradshaw, J. Am. Chem. Soc., 55, 1780 (1933).
8. R. J. Gale, B. Gilbert, and R. A. Osteryoung, Inorg. Chem., 17, 2728 (1978).
9. C. A. Angell, I. M. Hodge, and P. A. Cheeseman, in "Proceedings of the International Symposium on Molten Salts," J. P. Pemsler, J. Braunstein, K. Nobe, D. R. Morris, and N. E. Richards, Editors, p. 138, The Electrochemical Society Softbound Proceedings Series, Princeton, NJ (1976).
10. F. H. Hurley and T. P. Weir, J. Electrochem. Soc., 98, 203 (1951).